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The report describes work performed under Contract No. DAABO7 75-C-1770 for the design, construction, and testing of advanced state-of-the-art high rate stable vented nickel-cadmium batteries, with a special emphasis on the improvement of the separator wrap. Eagle-Picher Industries, Inc. designed and tested three to five cell units (BB-600 cells) of the BB-433 aircraft battery during phase I of this contract for the purpose of determining and selecting an optimum design. Phase II, the second half of the contract, included the design, fabrication and testing of 24 volt. 35 ampere-hour batteries of the BB-433.

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configuration, utilizing the optimum design features of phaseI. The batteries and the three to five cell units were tested in accordance with the updated Technical Guidlines For High Rate Stable Nickel-Cadmium Batteries dated 31 August 1976, U.S. Army ERADCOM. On the basis of the most critical tests namely temperature rise and float and low temperature - high rate pulse - Celgard 3400 and Permion 2291 (40/20) were the best replacements for the old standard cellophane wrap. On the basis of the life cycling test, Celgard 3400 was the best single layered separator. Although cells with a combination of Celgard 3400 and cellophane did not pass the low temperature - high rate tests, they exhibited the best cycle life performance.

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#### 1. Introduction

The vented nickel cadmium battery is one of the best known power sources in the commercial and military fields, particularly for aircraft and communications applications. It has excellent high rate and low temperature performance capabilities. In addition, it has a long useful life capability and is both physically and electrochemically rugged. However, a major shortcoming of present state-of-the-art vented nickel cadmium batteries is that the cellophane separator, which serves as an oxygen barrier to prevent thermal runaway, limits the life of the battery as a result of its steady degradation under oxidative attack. A secondary shortcoming is the problem of capacity loss by the recrystallization of cadmium and cadmium hydroxide at elevated temperatures at low rates of charge and discharge. This latter problem can be resolved by the addition of about 0.5% - 1.0% indium hydroxide to the active cadmium material and/or by special pulse-type charging methods (1,2).

Under a series of Air Force test programs, (3,4,5,6) very thin (1 mil thick) highly stable separators, having reasonably good electrical conductivities, have been developed as a substitute for cellophane in the vented nickel cadmium (NiCd) battery. They are cross-linked, and grafted with methacrylic acid on a base of low density polyethlene; known as P-2201 (40/30) and P-2291 (40/20) (the latter having the lower resistivity) they are manufactured by RAI Research Corporation Hauppauge, Long Island, NY. Aircraft Ni/Cd batteries with these separators have performed better than those with standard cellophane in terms of: (1) high temperature constant potential charging, and (3) high temperature discharging.

In recent years, another stable separator of good electrical conductivity, referred to as Celgard 3400 has been developed by the Celanese Plastics Company, Greer, SC. It is a 1 mil thick microporous polypropylene separator, coated with anionic/nonionic surfactant - the average pore size of the separator being about 200 Å. Celanese has developed this material to meet the stringent requirements of the vented Ni/Cd battery. Preliminary test results of Ni/Cd batteries with Celgard-type separators by the King Defense Research Establishment, Ottawa, Canada, were very promising, particularly at low temperatures (7).

#### Experimental and Test Procedures

#### 2.1 Scope

The design, construction and testing of the experimental vented nickel-cadmium batteries and battery cells of this program followed the "Technical Guidelines for High Rate Stable Nickel-Cadmium Batteries", dated 31 August 1976, U.S. Army ERADCOM. The prime variable was the separator and the test cell was the 35 Ah BB-433 vented nickel-cadmium aircraft battery. At the beginning of the program some work was done on additives to the cadmium anode for the purpose of minimizing fadeout or crystal growth of cadmium and cadmium hydroxide at elevated temperatures, utilizing the Eagle-Picher VNC 5.5 Ah vented nickel-cadmium cells. Thereafter, the work concentrated on developing and selecting a stable separator, using the BB-433 aircraft battery configurations. In both phases of the program the test results of the experimental units and batteries were directly compared with standard models containing cellophane separators.

# 2.2 Basic Cell Design (BB-600 Unit Cell)

The same basic cell design was employed in the BB-600 unit cell of the Phase I tests and the Phase II 24 volt BB-433, 35 Ah battery tests. The pertinent design features of the BB-600 unit cell were as follows: a) Ni(OH)<sub>2</sub> cathodes - 20 mil plates with a total theoretical capacity of 48 ampere-hours, said cathodes having 5% CO(OH) additive; b) Cd anodes - 20 mil plates with a total theoretical capacity of 80 ampere-hours, said anodes containing no additives; c) separator wrap-one or two layers of oxygen barrier-type membranes sandwiched between two layers of 3 mil thick woven nylon mesh; d) electrolyte - 31% KOH with 1% LiOH to a level in the cell which is slightly above the plates; e) other-nylon cell cases and covers which are welded together, said covers containing heavy duty nickel plated terminals with the nickel tabs of the electrodes being bolted to the bar of the terminals and the vent was of the bunsen-type.

#### 2.3 Test Procedure for Fadeout (5.5 Ampere-Hour-Cells)

The VNC 5.5 A cells were tested in accordance with the following procedure:

- A. Test cells were charged at 5.5 ampere constant current rate at room temperature (73°F) until an average cell voltage of 1.55 volts was reached. Test cells were then placed on a 1.1 ampere constant current charge rate for three (3) hours.
- B. Test cells were then discharged at 5.5 ampere constant current rate at room temperature (73°F) after a 20-minute stand. The cells were discharged to an average cell voltage of 1.00 volts.

- C. Test cells were then run down to zero (0) volts and each cell individually shorted and allowed to drain for 16 hours (minimum).
- D. Test cells were placed in a test chamber at  $125^{\circ}F \pm 2^{\circ}F$  and allowed to soak for four hours. They were then charged at a constant current rate of 69 ma. for 160 hours.
- E. Test cells were then transferred to a test chamber set to  $-20^{\circ}F$   $\pm~2^{\circ}F$  and allowed to soak for 16 hours (Overnight). Cells were then discharged at a one ampere constant current rate.
- F. Test cells were then discharged to zero (0) volts and each cell individually shorted and allowed to drain for 16 hours. (Minimum).
- G. Test cells were then charged as in A.
- H. Test cells were discharged as in B.

#### 2.4 Phase 1 Test Procedures (Three to Five Cell BB-600 Cells)

The 3-5 cell units were subjected to the following tests in the order shown in table 1 below. The sequence on the high temperature test and low temperature test was reversed on half of the test units. Fresh units were used for each sequence. Fresh units were employed for the automatic life cycling tests, as well as for the environmental tests 2 to 5 - the unit batteries being discarded after completion of the temperature rise and float test.

TABLE 1: Listing of Phase 1 Tests

1.	Test Initial Capacity	No. of Cells All
2.	High Temperature Test	5
3.	Low Temperature Test	5
4.	Low Temperature - High Rate	5
5.	Temperature Rise & Float	5
6.	Automatic Life Cycling	3-4

The Phase 1 test procedures are as follows.

# 2.4.1 Initial Capacity

Determine initial capacity of each 3 - 5 cell group by charging batteries at 35 amperes for one hour followed by a topping charge at 17.5 amperes for two hours and discharging at 35 amperes to an average 1.0 volt/cell cutoff. Use constant current d.c. (c.c.d.c.) as the charging mode and run capacity test at  $73^{\circ}F \pm 9^{\circ}F$ . Repeat the capacity test and take the average value of the two deep cycles as the initial capacity of the battery. All charge/discharge voltages are recorded.

#### 2.4.2 High Temperature Test

- a) Store battery in a test chamber at  $125^{\circ} \pm 2^{\circ}$ F for 16 hours.
- b) Charge at  $125^{\circ} \pm 2^{\circ}F$  at 35 amperes c.c.d.c., for one hour and then at 17.5 amperes for two hours.
- c) Rest 15 minutes at  $125^{\circ}F + 2^{\circ}F$ .
- d) Discharge at  $125^{\circ}F \pm 2^{\circ}F$ , at 35 amperes until an average cutoff of 1.0 V/cell.
- e) Repeat (a) (d) two times on cycles 2 and 3.
- f) Expected service on the third cycle is about 50 minutes.

#### 2.4.3 Low Temperature Test

- a) Store battery in a test chamber at -40° + 2°F for 16 hours (overnight).
- b) Charge at  $-40^{\circ} \pm 2^{\circ}$ F at 35 amperes c.c.d.c., for one hour and then at 17.5 amperes for two hours.
- c) Rest 15 minutes at  $-40^{\circ} \pm 2^{\circ}$ F.
- d) Discharge at  $-40^{\circ} \pm 2^{\circ}$ F at 35 amperes to an average cutoff of 0.90 V/cell. Repeat (a) (d) two times. Expected service at the second and third low temperature charge-discharge cycles is about 50 minutes.

# 2.4.4 Low Temperature - High Rate Test

- a) Store battery in a test chamber at 73° + 9°F for 16 hours (overnight).
- b) Charge at  $73^{\circ} \pm 9^{\circ}$ F at 35 amperes (c.c.d.c.) for one hour and then 17.5 amperes for two hours.
- c) Store at 0° + 2°F for 16 hours.
- d) Discharge 0° + 2°F as follows:
  - At about 750 amperes using a 0.0167 ohm resistance for 5 seconds immediately decrease current to
  - 2) 200 amperes for 15 seconds (total time: 20 seconds).
- e) Rest on OCV for 120 seconds.
- f) Repeat d) and e).
- g) Record voltages at 5 and 20 second periods. The 5-second voltage should be about a minimum average of 0.63 V/cell, and the 20-second voltage should be about a minimum average of 0.90 V/cell.

#### 2.4.5 Temperature Rise and Float Test

Charge the 3 to 5-cell groups per 2.4.1.

Store groups in a chamber at  $120^{\circ}$ F until temperature of the electrolyte in the cells reaches ambient temperature of the chamber. At this temperature, discharge battery at 9.0 C rate (315A) for 5 minutes. Immediately following this discharge with the battery still in the chamber at  $120^{\circ}$ F, a constant potential charge of 1.470  $\pm$  .01 V/cell shall be conducted for 50 hours. The battery will then be discharged at  $120^{\circ}$ F at the 1 C rate (35A) to 0.95 V/cell. Voltage, current, time and center cell electrolyte temperature shall be recorded throughout the test. The battery should deliver

about one hour or more of service. No water additions shall be made after placement of the battery in the chamber. Temperature readings taken in the center cell of the battery should not exceed  $160^{\circ}$ F during the above test; and after the initial current drop during float, the current should not rise more than 3 A above its steady state at any time during the test.

#### 2.4.6 Automatic Life Cycling

Cycle 200

After determining the initial capacity as per 2.4.1 (cycles 1,2) shallow cycle the batteries by c.c.d.c. charging at  $73^{\circ} \pm 9^{\circ}F$ . The automatic cycling procedure shall be as follows:

Cycle 3	Charge as per 2.4.1 Di	scharge at 35
	amperes for 36 minutes.	(21.0 Ah).

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Cycles 4-98	Charge at 15 A for 105 minutes. (26.5 Ah,
	26% overcharge). Discharge at 35 A for
	36 minutes.

Cycle 99	Charge at 15 A for 110 minutes. Discharge
	at 35 A to an average 1.0 V/cell for each
	3-4 cell. Thereafter discharge each cell
	at 10 A to 0.0 V/cell.

Cycle	100	Charge per 2.4.1.	Discharge	at	35 A	to an
		average 1.0 V/cell	for each	3-4	cell	group.

Cycles 101-198	Repeat procedure for cycles 4-98 above.
Cycle 199	As per cycle 99.

As per cycle 100.

Continue cycling in the same sequence as 101-200 until the cycle 100 capacity falls to 21 Ah or less, after each charge.

#### 2.5 Phase 11 Test Procedures (BB-433 Battery)

#### 2.5.1 Capacity Discharge

Charge batteries at 35 amperes for one hour followed by a topping charge at 17.5 amperes for two hours. Discharge at 35 amperes to a 20 volt cutoff. Use constant current d.c. (c.c.d.c.) as the charging mode and run capacity test at  $73^{\circ} \pm 9^{\circ}$  F. Repeat capacity test two times and take the average value of the last two cycles as the initial capacity of the battery.

#### 2.5.2 Twenty-Second Pulse Test (R. T.)

The battery is charged as per 2.5.1. After a charged stand of 16 hours at  $73^{\circ}F \pm 9^{\circ}F$  the battery is discharged at approximately 750 amperes  $(73^{\circ}F \pm 9^{\circ}F)$  into 0.0167 ohm load for 20 seconds, given a 2 minute rest and pulse again for 20 seconds, the pulse rest sequence being run for a total of three times. Voltages are recorded throughout this test. The minimum voltage on this test should be 10 volts, with 12 volts as the desired value.

# 2.5.3 Low Temperature High Rate Discharge (-22°F)

The battery is charged as per 2.5.1 and stored in an environmental test chamber at  $-22^{\circ}F \pm 2^{\circ}F$  for 24 hours, the temperature being recorded within the electrolyte of the center most cell and all electrical wiring outlets through the chamber being properly heat insulated prior to battery storage. Discharge the battery at 270 amperes at  $22^{\circ}F \pm 2^{\circ}F$  to 0.684 V/cell average (13.0 volts for a 19 cell battery). The following is to be recorded:

- 1) The terminal voltage, 5 seconds after the start of discharge.
- 2) The elapsed time to the end voltage (0.684 V/cell) after the start of discharge. Service of 3 minutes or more and a 5-second voltage of 13 volts or higher are required.

#### 3. Preliminary Results on Fadeout Tests

Whereas the degradation of the standard cellophane separator has been the primary failure mode of vented nickel-cadmium batteries, capacity loss by fadeout of the cadmium and cadmium hydroxide usually occurs on float or standby service and during low rate discharge, particularly at elevated temperatures. F.G. Will and H.J. Hess (8) have deomonstrated that the migration of a soluble cadmium species from the interior of the plate to the plate surface is accompanied by an increase in the size of the particles, and Y. Okinaka (9) has shown that the rate of particle growth increases with increasing temperature and decreasing rates of discharge. The capacity loss of the cadmium anodes has been shown to be reduced by the addition of a small amount of Fe<sub>2</sub>0<sub>3</sub> to the cadmium anode (10), or by the addition of a small amount of indium to the active cadmium during the impregnation process (11) or by a 1% addition of In(OH)<sub>3</sub> by weight to the active cadmium oxide mix in mold pressed plates (1).

As a followup of the indium work, preliminary tests were carried out on 10 cell C.P. VNC-5.5A cells having sintered type cadmium anodes of three variations as follows: a) anodes with 1% In(OH)<sub>2</sub> additives introduced via standard nitrate impregnation process; b) pure cadmium anodes and c) anodes with a small percentage of proprietary additive.

The ratio of cadmium active material to that of nickel hydroxide was lower than in the standard batteries so that cadmium limiting conditions could be more readily observed and controlled.

Employing the test procedures of section 2.1, the resulting discharge curves are plotted in figures 1 - 3, figure 1 represents the initial

discharge curves of the unit at the C rate of discharge. No major difficulties are noted in the performances of the three 10 cell batteries - the cell potentials in the 3 curves representing the average of the 10 cell batteries.

Figure 2 shows the -20°F, 1 ampere rate discharge curves of the three batteries after the units had been subjected to the 125°F fadeout regime. Here the beneficial effect of the indium coated anodes is clearly demonstrated; i.e., the capacity of the indium units was 1.00 Ah to a 1.0 volt cutoff at a closed circuit potential of 1.15 volts per cell, versus 0.42 Ah at about 1.14 V/cell for the pure cadmium unit and 0.37 Ah at about 1.08 V average for the cells with the proprietary additive.

Figure 3 shows the restored performances after the fadeout - low temperature sequence of tests. The figure shows that the 10 cell units suffered no permanent loses as the performances were comparable with that of the initial discharges.

Other performance characteristics of the indium doped 10 cell units are shown in figures 4 through 7, the performances of which are compared with a 10 cell unit containing standard anodes with the proprietary additive, Figure 4 shows the charge potential per cell of the two units charged at the 5 ampere rate at 75°F. The subsequent discharge at the 15 ampere rate at 75°F is shown in figure 5. The 15 ampere discharge curves at -40°F of the two units are shown in figure 6, and the 15 ampere discharge curves at 125°F are shown in figure 7, from these data it can be seen that; a) the low temperature discharge of the indium doped units displays a significantly higher capacity and potential than the standard unit. b) The performances of the two units at 75°F and 125°F are equivalent and c) the overcharge potential of the indium cells is about 0.05V lower than that of the

### AVERAGE CELL VOLTAGE

1.000 1.05 ... 1.15 1.20 1.35 1.25 1.30 5 5.5 A Discharge @ 73° . INDIUM DOPED NEC. STANDARD 20 PURE CADMIUM 30 5 50 60 70 80 90

DISCHARGE TIME

(MINUTES)

FIGURE I
INITIAL DISCHARGE CURVES
OF THREE NI/Cd VNC 5.5 AH, CELLS
AS A FUNCTION OF ANODE ADDITIVES

# AVERAGE CELL VOLTAGE

T. 00 .15 1.05 == 1.20 1.25 1.30 1.35 5 20 30 5 50 60 STANDARD IA DISCHARGE @ -200F \_.\_INDIUM DOPED NEG --- PURE CADMIUM 70 80 90

(MINUTES)

TIME

FIGURE 2

LOW TEMPERATURE DISCHARGE CURVES OF THE 10 CELL VNC 5.5 AH NI/Cd UNITS AS A FUNCTION OF ANODE ADDITIVE

. 00 1.05 : 10 <del>.</del> 15 1.20 1.25 1.30 5 20 \_\_\_INDIUM DOPED NEG 5.5 A DISCHARGE @ 73°F STANDARD -PURE CADMIUM 30 40 (MINUTES) TIME 50 60 70 80 90

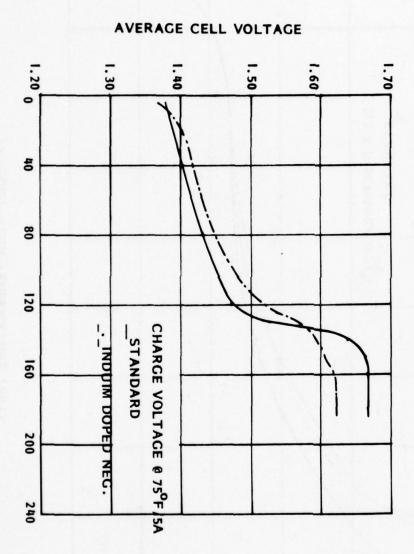
00

ONE HOUR RATE DISCHARGE CURVES OF THE IO CELL VNC 5.5 Ah NI/Cd UNITS AS A FUNCTION OF ANODE ADDITIVES AFTER COMPLETION OF THE FADEOUT - LOW TEMPERATURE TESTS

FIGURE 3

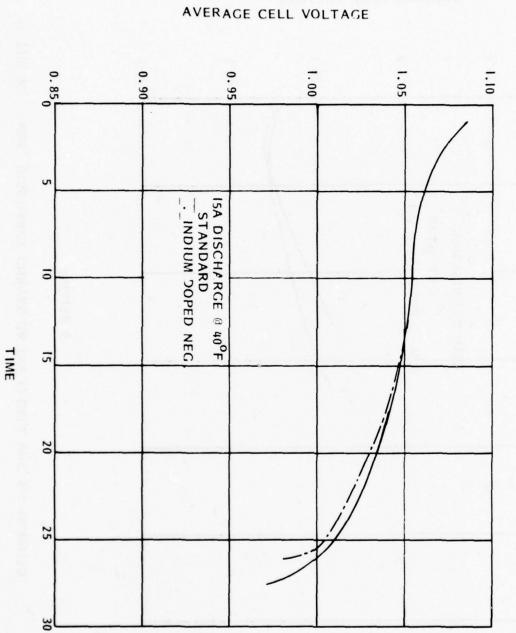
FIGURE 4

CHARGING CHARACTERISTICS OF THE 10 CELL VNC 5.5 Ah Ni/Cd UNITS AS A FUNCTION OF ANODE ADDITIVE



TIME (MINUTES)

FIGURE 5



(MINUTES)

15

# AVERAGE CELL VOLTAGE

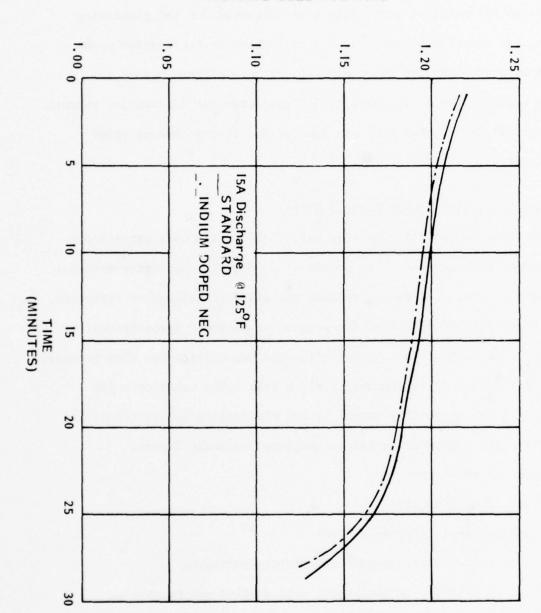
0,90 0.95 1.00 1.05 :-5 \_. INDIUM DOPED NEC. STANDARD ISA DISCHARGE @ -40PF 5 TIME (MINUTES) 5 20 25 30

THE 3C , -400F, DISCHARGE CURVES OF THE 10 CELL VNC 5.5 Ah UNITS

FIGURE 6

FIGURE 7

# AVERAGE CELL VOLTAGE



17

standard cells (again, all potentials in figures 1-7 represent the average of the 10 cell units).

These preliminary tests on fadeout indicates that there is a practical resolution to the problem, especially after more work on the processing techniques and after optimizing the indium content in the cadmium anode. It should be noted that the major emphasis of this program was on the separator system. Due to the severity of the separator degradation thermal runaway problem, no further work was carried out in the fadeout study in this contract.

### 4. Results and Discussion of the Phase I Tests

These tests on the three to five cell BB-600 units were carried out as a screening procedure so as to arrive at an optimium separator wrap for BB-433 battery. The goal was to replace the standard cellophane separator, which is vulnerable to oxidative degradation at elevated temperatures, by a separator that is resistant to oxidation and degradation but also possesses the desired features of cellophane; i.e., a high ionic mobility a low resistivity, is dimensionally stable in KOH electrolyte and is relatively inexpensive. The separator variations employed in phase I were:

- a) One layer of cellophane
- b) One layer of Celgard 3400
- c) One layer of Permion P-2291 (40/20)
- d) Same as c) but with the special electrolyte additive.
- e) One layer of E-6001. (A metacrylic acid grafted polypropylene, noncross-linked, membrane developed by RAI Research Corporation).
- f) One layer of Celgard 3400 plus one layer of cellophane (facing the anode).
- g) One layer of E-6001 plus one layer of cellophane (on the anode side).
- h) A blank no membrane between the two layers of woven nylon.

It should be noted that all electrode packs were of the same internal cell pressure of about 1 to 3 PSIG in the electrolyte activated cell. This was accomplished by the removal of one end anode and shimming each cell to the same electrode pack thickness, thereby compensating for the variations in separator thicknesses.

In addition no electrolyte additives, except for 1% LiOH was employed in any of the 3-5 cell units, the exception being the design where a special cadmium anode stabilizer was used.

After meeting the initial capacity tests the 3-5 cell units were subjected to the phase I tests as listed in table 1 (section 2.4).

#### 4.1 High Temperature Test

After 3 initial capacity tests the experimental units were given three cycles at  $125^{\circ}F$  (on charge and discharge). The third cycle capacities of the initial capacity tests and the third cycle capacity of the  $125^{\circ}F$  tests are shown in table 2, also included are the 3rd cycle  $20^{\circ}F$  test results.

The data in table 2 indicates no major difference in performance between the various designs. All units had excellent capacities at room temperature and at  $-20^{\circ}F$ . The slightly lower  $125^{\circ}F$  capacities of the composite designs (g) and (h) are not understood. The 26.2 Ah value of the blank at  $125^{\circ}F$  is surprisingly high since it has no oxygen barrier.

# 4.2 Low Temperature Test (-40°F)

After the three  $-20^{\circ}$ F cycles the experimental units were subjected to three  $-40^{\circ}$ F cycles using the same charge/discharge regime employed in the preceeding cycles.

TABLE 2
INITIAL, 125°F and -20°F CAPACITIES of THE 5.5 Ah VNC UNITS

CHARGING: 35A for 1 Hour, followed by 2 hours at 17.5 A

DISCHARGING: 35A to 1.0 V/Cell

g) 1 E-6001 + 1 Cello		f) 1 Celg 3400 + 1 Cello	e) LT-10	d) E-6001	c) P-2291 (40/20)	b) Celgard 3400	a) Cellophane	DESIGN
42.5	ello 44.6	1 Cello 43.4	48.0	47.5	44.5	46.0	42.5	INITIAL 75°F CAPACITY (Ah)
26.2	26.2	26.4	32.8	30.8	28.7	28.9	29.7	$\frac{125^{O}F}{CAPACITY}(Ah)$
39.8	38.2	38.0	40.8	43.3	42.7	42.6	41.8	-20°F CAPACITY (Ah)

The discharge curves of the single membrane layered units on the first, second and third cycles at -40° F are shown in figures 8, 9 and 10. All discharges were carried out beyond the knee of the discharge curve to determine the total cell capacities as well as the complete voltage characteristics. In figure 8 it can be seen that the cellophane control was virturally inoperable, the average cell potential never having exceeded 0.8 volts. The retained capacity to 0.5 volt/cell of the cellophane design was 16 Ah. These test results suggest that the failure of the cellophane controls at -40°F was most likely due to the presence of carbonate and cellulosic degradation products that had been generated during the 3 cycles 125°F, a temperature at which the cellulose is readily oxidized and cleaved in alkaline electrolytes (1) (10). In the case of the Celgard 3400 design there was a significant initial dip in cell potential, while the retained capacity was at 26Ah to 0.5 volt/cell. The initial potential dips of the Celgard 3400 design may be due to a temporary "fadeout" condition in the cadmium anodes, since this dip was erased on the following -40°F cycle (shown in figure 9). It should be noted that the first cycle -40°F dip potential of the Celgard 3400 cells represent the only negative response of all phase 1 and 11 test of this design. The first cycle -40°F discharge curves of the P-2291 (40/20), E-6001 and LT-10 units were excellent, i.e., their capacities were in a range of 28.5 Ah (LT-10) to 31.5 Ah (P-2291 (40/20)) to 1.00 V/cell and the ccvs were between 1.08 volts/cell (P-2291 (40/20)) and 1.12 volts/cell (LT-10).

In figure 9, the second -40°F cycle, the cellophane unit was still seriously impaired, although somewhat improved over the first

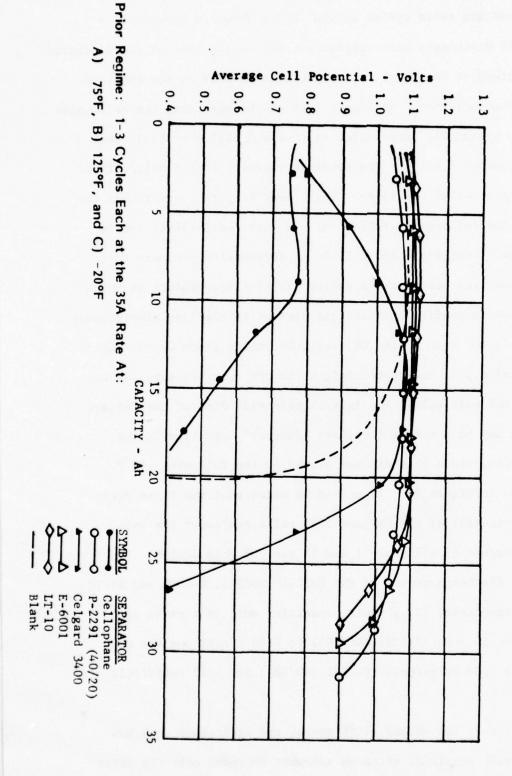
LOW TEMPERATURE PHASE I TESTS (FIRST CYCLE) - SINGLE MEMBRANE DESIGNS FIGURE 8

Charge: 35A For 1 Hour, Followed By 17.5 A For Two Hours

Discharge: 35A To End of Knee

Temperature: -40°F On Charge and Discharge

Battery: 3-4 Cell Units of the BB-433



1

LOW TEMPERATURE PHASE I TESTS (SECOND CYCLE) - SINGLE MEMBRANE DESIGNS

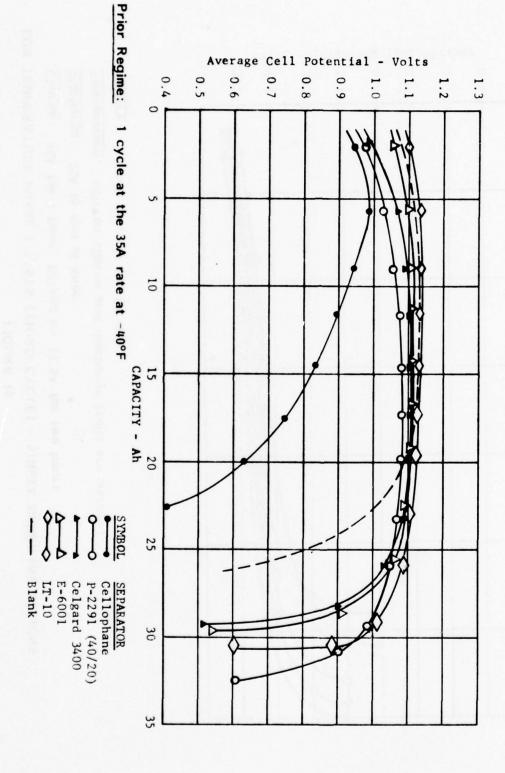
FIGURE 9

Charge: 35A for 1 hour, followed by 17.5A for two hours

Discharge: 35A to end of knee

Temperature: -40°F on charge and discharge

Battery: 3-4 cell units of the BB-433



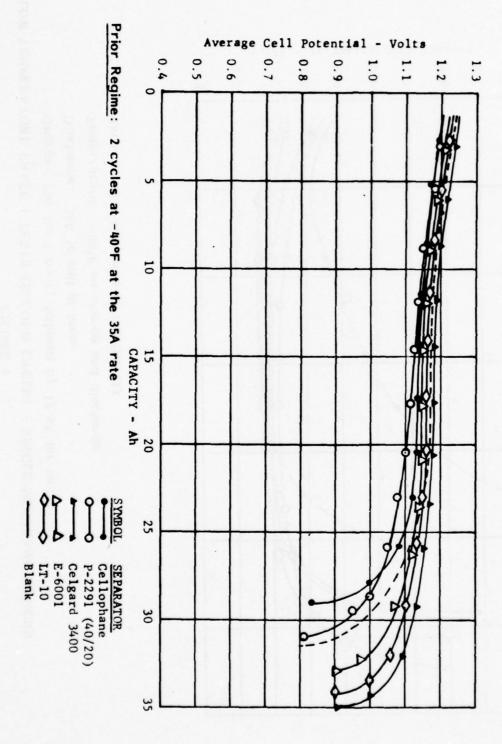
LOW TEMPERATURE PHASE I TESTS (THIRD CYCLE) - SINGLE MEMBRANE DESIGNS FIGURE 10

Charge: 35A for 1 hour, follwed by 17.5A for two hours

Discharge: 35A to end of knee

Temperature: 40°F on charge and discharge (cells are warmer)

Battery: 3-4 cell units of the BB-433



cycle i.e., the capacity to 0.5 volt/cell was 22 Ah and the "peak" potential was 0.99 V/cell - there being no plateau potential. By comparision, the blank has a capacity of 26 Ah to 0.5 V/cell (23 Ah to 1.00 V/cell) and a ccv of 1.12 volts/cell. The second cycle -40°F discharge curves of the Celgard 3400 P-2291 (40/20), E-6001 and LT-10 units were excellent i.e., the capacities were in a range of 27.5 Ah (Celgard 3400 and E-6001) to 29.5 Ah (P-2291 (40/20) and LT-10) to 1.00 volt/cell (LT-10).

In figure 10 the third and final cycle at -40°F, the performance of all the units, including the cellophane design, were excellent. Since the experimental units were run continuously and without any significant rest period, it is quite likely that the improved performances were partly due to an increase in the internal cell temperature above -40°F.

The high temperature - low temperature test sequence employed in phase 1 provides a practical screening method for separators. Under standard battery test procedures the high temperature tests normally follows the low temperature tests, and thereby the standard cellophane batteries pass both tests with excellent performance characteristics, as do other batteries with marginal separators. However, with the reverse sequence of tests, the marginal batteries are conditioned during the high temperature regime to be vulnerable on the following low temperature test. This sequence is therefore the preferred method for screening Ni/Cd battery separator designs.

Figures 11, 12, and 13 show the first, second and third  $-40^{\circ} F$  cycles of the composite Celgard 3400/cellophane membranes - using the

same performance curves of the single layered cellophane and Celgard 3400 units of the preceding figures. Figure 11, shows that the performance of the composite design is between those of the component designs. This pattern continues through the second and third cycles (figures 12 and 13). Figures 11-13 show that the excellent performance features of the single layered Celgard 3400 design significantly carry over to the composite design, but not sufficiently to overcome the short comings of the weaker cellophane design. The Celgard 3400 layer apparently offers a considerable amount of protection to the cellophane layer from oxidative attack and degradation. However, the relatively large pore size of Celgard 3400 - 200 Å in length - does not completely block the transport of dissolved oxygen from the nickel cathodes on overcharge towards to cellophane layer and therefore some degradation does occur.

Figures 14, 15 and 16 show the first, second and third -40° F cycles of the composite E-6001/cellophane design along with those of its component membranes. As with the Celgard 3400/cellophane curves of the preceding three figures, the performance curves of the single layered cellophane and E-6001 units are taken from figures 8-10. Figure 14 (first -40°F cycle) shows that E-6001 offers considerably more protection to cellophane from oxidative attack than that of Celgard 3400 (by comparing figures 14 and 11). The figure shows that the performance of the composite nearly matches that of the strong E-6001 component. This effect is further demonstrated in the second and third -40°F cycles, shown respectively in figures 15 and 16. The beneficial effect of the E-6001 layer on cellophane is attributed

LOW TEMPERATURE PHASE I TESTS (FIRST CYCLE) - CELGARD 3400/Cellophane Composite FIGURE 11

Control of the second

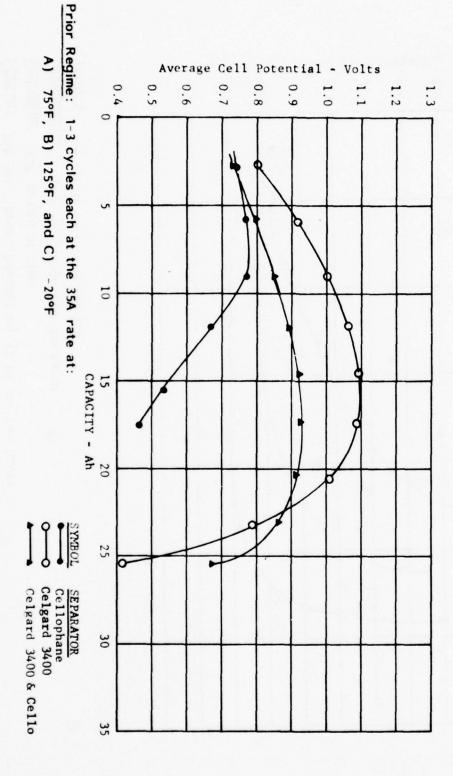
Charge: 35A for 1 hour, followed by 17.5A for two hours

Discharge: 35A to end of knee

Discharge: 35A to end of knee

Temperature: -40°F on charge and discharge

Battery: 3-4 cell units of the BB-433



LOW TEMPERATURE PHASE I TESTS: (SECOND CYCLE) - CELGARD 3400/Cellophane Composite FIGURE 12

Charge: 35A for 1 hour, followed by 17.5A for two hours

Dishcarge: 35A to end of knee

Temperature: -40°F on charge and discharge

Battery: 3-4 cell units of the BB-433

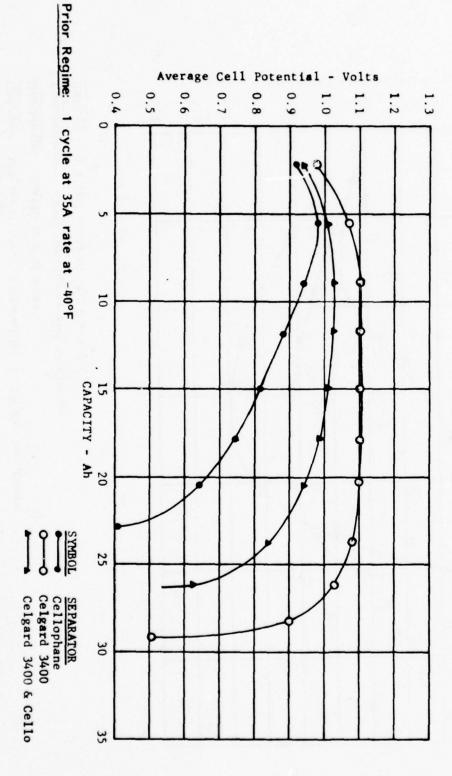


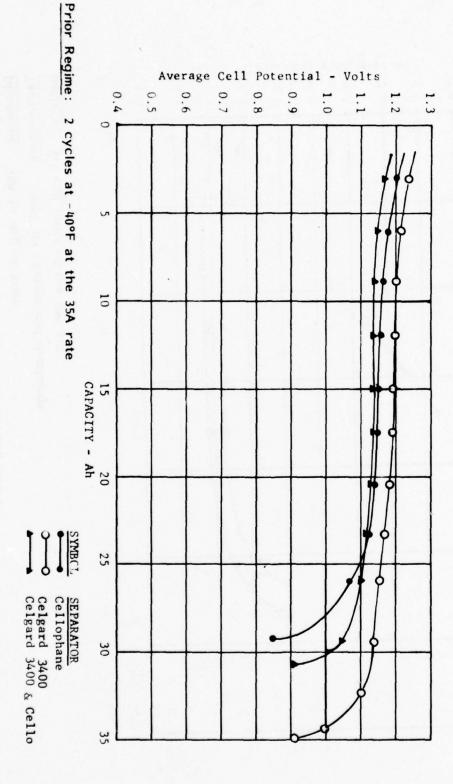
FIGURE 13

LOW TEMPERATURE PHASE I TESTS: (THIRD CYCLE) - CELGARD 3400/Cellophane Composite

Charge: 35A for 1 hour, follwed by 17.5A for two hours

Discharge: 35A to end of knee

Temperature: -40°F on charge and Discharge (cells are warmer)

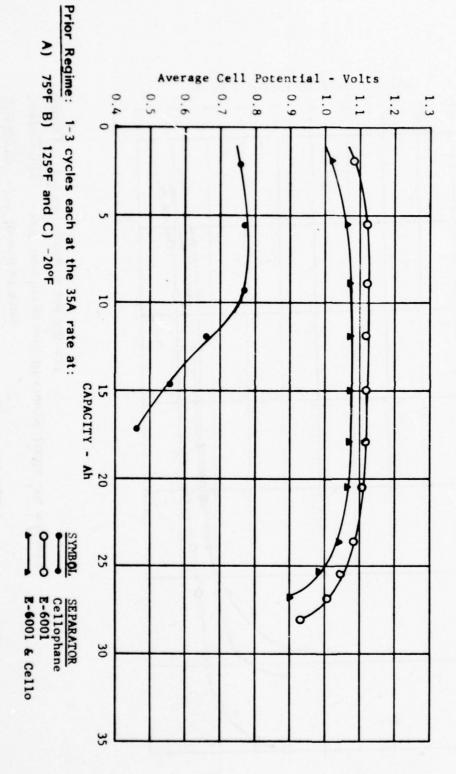


LOW TEMPERATURE PHASE I TESTS (FIRST CYCLE) - E-6001/Cellophane Composite FIGURE 14

Charge: 35A for 1 hour, followed by 17.5A for two hours

Discharge: 35A to end of knee

Temperature: -40°F on charge and discharge

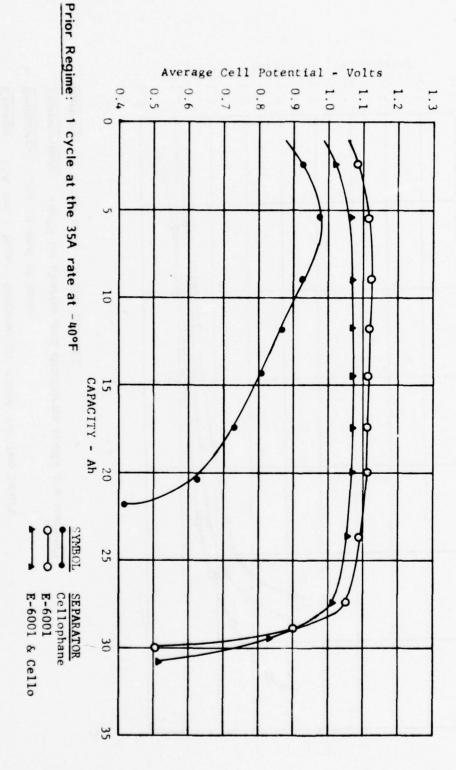


LOW TEMPERATURE PHASE I TESTS: (SECOND CYCLE) - E-6001/Cellophane Composite FIGURE 15

Charge: 35A for 1 hour, followed by 17.5A for two hours

Discharge: 35A to end of knee

Temperature: -40°F on charge and discharge

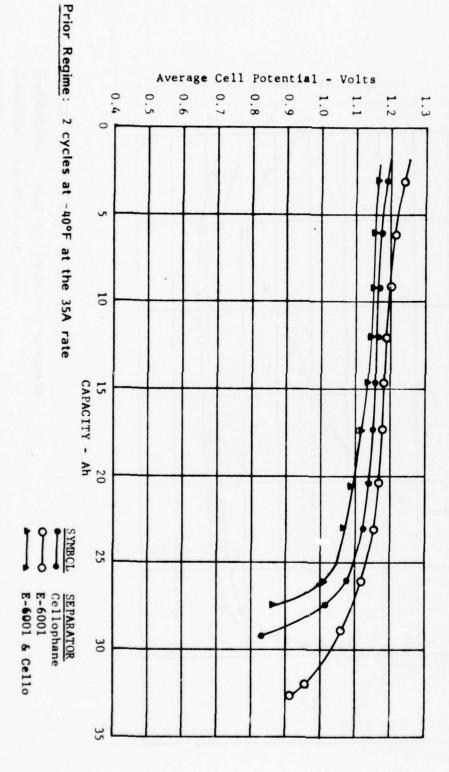


LOW TEMPERATURE PHASE I TESTS: (THIRD CYCLE) - E-6001/Cellophane Composite FIGURE 16

Charge: 35A for 1 hour, followed by 17.5A for two hours

Dishcarge: 35A to end of knee

Temperature: -40°F on charge and discharge (cells are warmer)



to the small effective pore size of E-6001, about 15  $^{\circ}A$  - 20  $^{\circ}A$ , which provides an excellent barrier to the "transport of oxygen". On the basis of the results shown in figures 14-16 it can be assumed that the E-6001/cellophane composite design should have a long cycle life on the Automatic Life Cycling Test.

## 4.3 The Low Temperature Test (-40°F) with No Prior High Temperature Exposure

Several of the separator designs were evaluated on the -40°F test without any prior high temperature testing. The purpose here was to determine the contrast in cell performance at -40°F with (see figure 8-16) and without any prior high temperature exposure. The -40°F discharge curves for the single membrane cellophane, P-2291 (40/20) and Celgard designs are plotted in figure 17. The figure shows flat discharge curves at a ccv range of 1.10 volts to 1.11 volts per cell. For the three designs, the capacities were excellent, with a range of 30 Ah to 32Ah to a 1.00 volt/cell cutoff. These data clearly demonstrate that the prior high temperature cycling at 125°F was solely responsible for the poor performances of the cellophane design at -40°F as shown in figures 8-10.

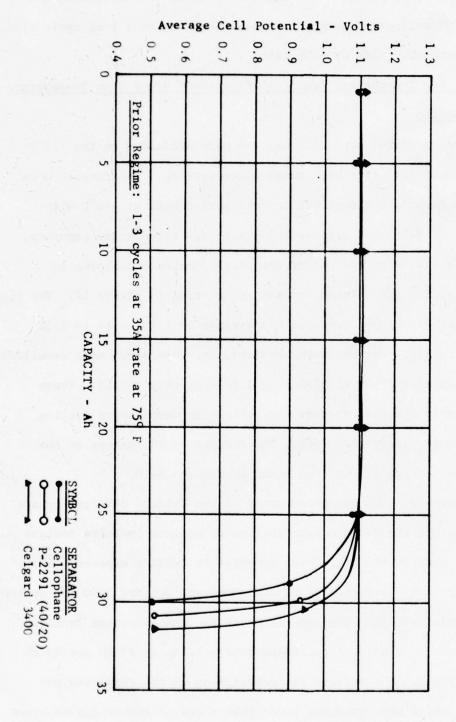
Figure 18 shows the performance of the Celgard 3400/cellophane composite and the K-306 Celgard/cellulose acetate laminate designs at -40°F without the prior high temperature cycling exposure. For comparison, the performances of the component Celgard 3400 and cellophane design are included. The capacities of the composite and laminate designs are very good, i.e., respectively being at 27 Ah and 29 Ah to 1.0 V/cell. The voltage characteristics of the composite and laminate cells were somewhat lower than those of the single membrane

FIGURE 17

Low Temperature Phase I Tests - No Prior High Temperature Exposure (Single Membrane Designs)

Charge: 35A for 1 hour followed by 17.5 A for two hours Discharge: 35A to end of knee

Temperature: -40° F on charge and discharge Battery: 3-4 cell units of the BB-433

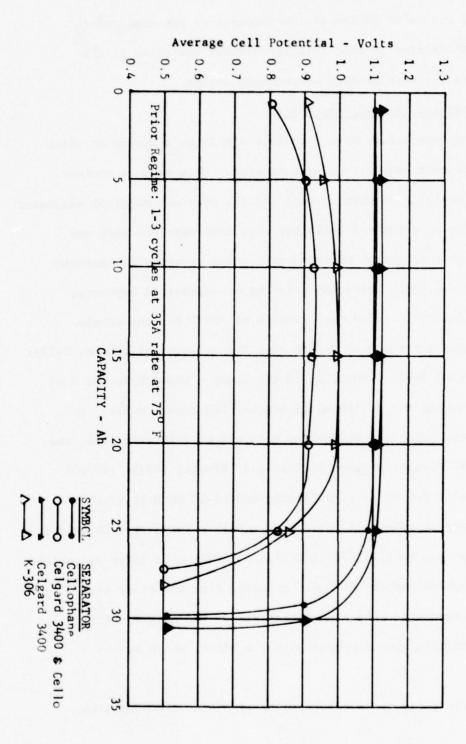


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FIGURE 18

Low Temperature Phase I Tests - No Prior High Temperature Exposure (Composite and Laminate Designs)

Charge: 35A for 1 Hour followed by 17.5 A for two hours Discharge: 35 A to end of knee
Temperature: -40° F on charge and discharge
Battery: 3-4 cell units of the BB-433



cells, the ccv's being at 0.93 volt/cell for the composite design and 1.00 volt/cell for the laminate design. The voltage characteristics of the K-306 design at low temperature are expected to improve with cycling in that this improvement was noted at the room temperature life cycling of the same design.

#### 4.4 Low Temperature High Rate Tests

The low temperature High Rate Test simulates a severe cranking test for aircraft and helicopter batteries. This test is another service screening procedure to weed out the poor and marginal separator designs. The experimental units for this test were the same one that had gone through the environmental tests reported in sections 4.1 and 4.2 i.e., all units had prior high temperature exposure.

The first cycle pulse test results at -20°F for the single membrane units are shown in figure 19. All units - cellophane, P-2291 (40/20) Celgard 3400, E-6001, LT-10 the blank - were above the 0.63 volt spec. during the following 15 second, 200 ampere pulse. On the 750 ampere pulse the cellophane unit was at 0.75 volt/cel1; the blank at 0.84 V/cel1; Celgard 3400 at 0.87 V/cel1; P-2291 (40/20) at 0.78 V/cel1; E-6001 at 0.82 V/cel1; and LT-10 at 0.79 V/cel1. On the 200 ampere pulse all units were within a range of 1.06 volts/cel1 (cellophane) to 1.12 V/cel1 (Celgard 3400). The lower potentials of the cellophane control no doubt resulted from the prior high temperature exposure. The high potentials of the Celgard 3400 design is striking when compared with the blank, which has no membrane.

The first pulse cycle test results at 0°F on the composite

Celgard 3400/cellophane and E-6001/cellophane designs are shown in figure 20. The test results of the cellophane, Celgard 3400 and E-6001 are shown on figure 19. At the end of the 750 ampere pulse the E-6001/cellophane was at 0.60 V/cell, or 0.03 V/cell, or barely over spec. On the 200 ampere pulse both compsoites met the 0.95 V/cell spec, but at considerably lower potentials than the cells with the component membranes.

It should be noted that the long cycle life capability of the composite designs make them more suitable for applications requiring a moderate rate of discharge, such as employed for communication and electronic devices. For high rate low temperature applications such as required for the BB-433 aircraft battery, the most suitable candidates are the stable single membrane designs; i.e., either the Celgard 3400 or P-2291 (40/20) designs.

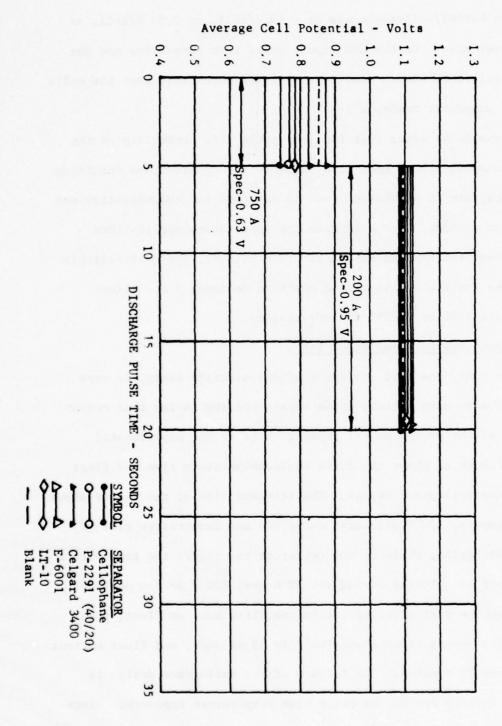
#### 4.5 Temperature Rise and Float Tests

This test, the most stringent of the aircraft tests, is very destructive to many battery grade separators and is for that reason the last of the environmental phase I tests on the experimental units. Figure 21 shows the first cycle temperature rise and float data of the cellophane design. The lefthand side of the figure shows the 315 ampere, 120°F discharge curve (v) and temperature rise (t) of the unit cells, while in the center of the figure the temperature and current are plotted during the 50 hours, 120°F period on float. The cellophane design failed within the first hour on float, the temperature having risen above 160°F in 55 minutes, and float current being above 12 amperes. The failure of the cellophane design is no doubt largely due to the prior high temperature exposure. Since

PHASE I LOW TEMPERATURE HIGH RATE TESTS (FIRST CYCLE) - SINGLE MEMBRANE DESIGNS Charge: 35A for 1 hour, followed by 17.5A for 2 hours (at73°F ± 9°F) FIGURE 19

Discharge: As shown

Temperature: 0°F ± 2°F

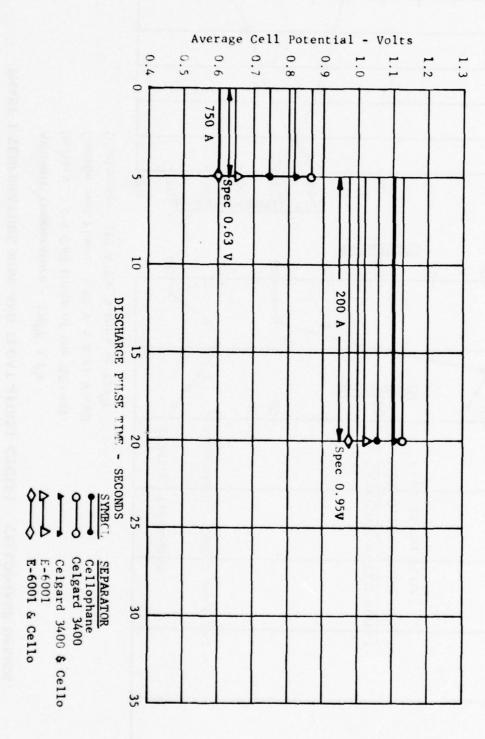


PHASE I LOW TEMPERATURE HIGH RATE TESTS (FIRST CYCLE) - COMPOSITE DESIGNS FIGURE 20

Charge: 35A for 1 hour, followed by 17.5A for 2 hours (at 73°F ± 9°F)

Dishcarge: As shown

Temperature: 0°F ± 2°F



0.50 0.80 0.90 0.40 0.60 0.70 1.10 8 0 DISCHARGE TIME (MINUTES) < Charge and Float: 1.47 V ± 0.01 V/cell Battery: 3-4 Cell Units of the BB-433 Discharge: 315 A for 5 Mins at 120°F U 170 -5 120 130 E TEMPERATURE 180 CURRENT -A 40 80 30 00 8 70 8 5 30 CHARGE TIME (MINUTES) CURRENT-A 30 Separators - Cellophane (Control) 55 Mins, Terminated FAILURE ON FLOAT NOT DISCHARGED DUE TO CAPACITY AFTER FLOAT: 5 FLOAT TIME (HOURS) 40

ᇹ

120

40

CELL

TEMPERATURE

170%

180

8

AVERAGE CELL

POTENTIAL-VOLTS

PHASE I TEMPERATURE RISE AND FLOAT (FIRST CYCLE) - CELLOPHANE DESIGN FIGURE 21

Ambient Temperature - 120°F ± 1°F

fresh nickel-cadmium batteries with cellophane pass the test without much difficulty, the prior high temperature treatment of the units and their practicality by the results of this important test.

Figure 22 shows the temperature rise and float data of the P-2291 (40/20) design (the following figures on temperature rise and float being plotted in the same manner as in fig 22). The data in figure 22 show that the P-2291 (40/20) design passed the temperature rise and float test with superior performance characteristics; ie., the cell temperatures never exceeded 150°F during the initial high current surge on float, the temperature leveled off at 120°F after 5 hours on float, and the current leveled off at 1.0 ampere during the 50 hour float regime. On the basis of this and the other phase I tests Permion P-2291 (40/20) was selected as a prime candidate for the phase II BB-433 battery tests.

Figure 23 shows the temperature rise and float data of the Celgard 3400 design. As with the P-2291 (40/20) design, the Celgard 3400 cells passed this test with excellent performance characteristics, although they sustained a float current at 2 amperes and the cell temperature on float at 125°F was slightly higher than those of P-2291 (40/20). For the same reasons given for the P-2291 (40/20) design, the Celgard 3400 design was selected as a prime candidate for the phase II BB-433 battery tests.

Figure 24 shows the temperature rise and float data of the E-6001 design. In this case the unit cells failed after 7 hours on float, the temperature having risen above 170°F while the current climbed to about 25 amperes - a condition encountered at the onset

0.80 0.90 0.40 0.50 0.60 0.70 8 5 0 DISCHARGE TIME (MINUTES) < G 170 E 120 130 E TEMPERATURE 180 ₹ Discharge: 315 A for 5 Mins at 120°F Charge and Float: 1.47 ± 0.01 V/cell Battery: 3-4 Cell Units of the BB-433 Ambient Temperature - 120°F ± 1°F CURRENT - A 80 00 20 30 50 70 5 CHARGE TIME (MINUTES) 30 CAPACITY AFTER FLOAT: 30 600 SEPARATOR -5 P-2291 (40/20 FLOAT TIME (HOURS) 0.95 V/Ce(I) 6

CELL

TEMPERATURE

180

ā

120

42

AVERAGE CELL POTENTIAL-VOLTS

PHASE I TEMPERATURE RISE AND FLOAT (FAST CYCLE) P-2291 (40/20) DESIGN FIGURE 22

0.80 0.90 0.40 0.50 0.60 0.70 ... 8 0 DISCHARGE TIME (MINUTES) < S 1170 ē 120 30 ELL TEMPERATURE 180 CURRENT - A 80 30 6 50 8 70 20 0 0 (MINUTES) 30 CURRENT-A 30 600 5 SEPARATOR 28.20 Ah (35 A Rate CAPACITY AFTER FLOAT: 5 CELICARD 3400 FLOAT TIME (HOURS) (2,0A) to 0.95 V cell) 40 8

AVERAGE CELL POTENTIAL-VOLTS

PHASE I TEMPERATURE RISE AND FLOAT (FIRST CYCLE) CELGARD 3400 DESIGN Ambient Temperature - 120°F ± 1°F FIGURE 23

Charge and Float: 1.47 V ± 0.01 V/cell

Battery: 3-4 Cell Units of the BB-433

Discharge: 315 A for 5 Mins. at 120°F

30 CELL

TEMPERATURE

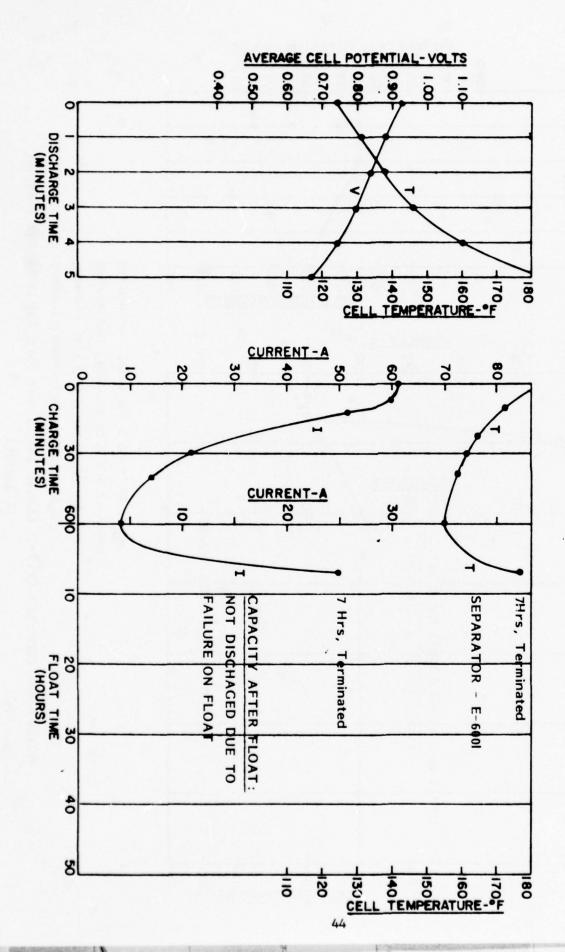
081

170%

120

ē

PHASE I TEMPERATURE RISE AND FLOAT Dishcharge: 315 A for 5 Mins. At 120°F Charge and Float: 1.47 V ± 0.01 V/cell Battery: 3-4 Cell Units of the BB-433 Ambient Temperature - 120°F ± 1°F FIGURE 24 (FIRST CYCLE) E-6001 DESIGN



of thermal runaway. An examination of the dissected cells showed that the E-6001 membrane had completely disintegrated into a gellike substance. The fact that E-6001 is not crosslinked, as is the case with P-2291 (40/20), is believed to be the reason for its rapid degradation in this test. As a result of this test failure E-6001 was eliminated from further consideration in this program.

Figure 25 shows the temperature and float data of the LT-10 design. This design failed after 40 hours on float. This membrane like E-6001, also was not uncrosslinked and was severely degraded. Therefore, it was eliminated from further consideration.

As a final note on the temperature rise and float tests table 3 below presents the capacity data of this test; i.e., the capacity retained by each design after the 50 hours,  $120^{\circ}$ F float regime.

Table 3; Retained Capacities after the Temperature Rise and Float Regime.

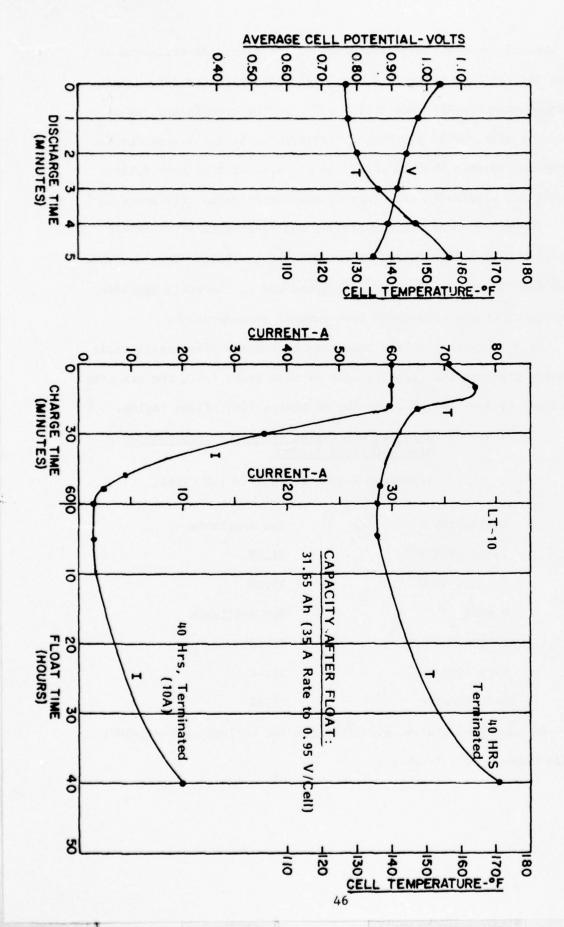
Discharge - 35 A at 75°F to 1.0 V/cell

Cellophane	Not available
P-2291 (40/20)	32.38
Celgard 3400	28.20
E-6001	Not available
LT-10	31.65
Celg 3400/Cello	33.48
E-6001/Cello	26.85

No capacity data was available for the cellophane and E-6001 units because of soft shorts.

PHASE I TEMPERATURE RISE AND FLOAT (FIRST CYCLE) LT-10 DESIGN Discharge: 315 A for 5 Mins at 120°F Charge and Float: 1.47 V ± 0.01 V/cell Battery: 3-4 Cell Units of The BB-433 Ambient Temperature - 120°F ± 1°F

FIGURE 28



#### 4.6 Automatic Life Cycling Tests

Fresh units of the more promising designs were placed on the automatic life cycling regime. The pertinent test procedures and cycle data are shown in table 4. The following designs were employed; a) cellophane, b) P-2291 (40/20) (no additive), c) P-2291 (40/20) (with special additive, d) K-306, e) Celgard 3400, and f) Celgard 3400/cellophane and g) E-6001/cellophane. Under each design are listed the capacities on the third deep cycle after approximately 100 shallow cycles. Also listed are the cycle numbers at which point any particular cell failed by shorting.

The data in table 4 indicate the following; a) the longest useful life was with the composite Celgard 3400/cellophane design (greater than 3100 cycles), b) the longest cycle life with a single layered spearator design was with Celgard 3400 (up to 2085 cycles) and c) runnerup on cycle life performance was the K-306 design (up to 2085 cycles with 1 short on cycle 1152). It should be noted that the voltage characteristics on charge and discharge were virtually the same for all designs.

Upon completion of phase I of this program it appears that Celgard 3400 is the best available, state-of-the-art single layering separator for the BB-433 aircraft battery or for any other high rate vented nickel-cadmium battery.

Table 4 - Life Cycling Data of the 3-4 Cell 35 AH BB-600 Units

Regime: 3 deep cycles after 97 shallows at 62% depth of discharge - at room temperature ambient. NOTE: After each first deep cycle the cells were drained at the 10 A rate to 0.0 V/cell in order to erase "memory".

Shallow Cycling: Charge at 15 A for 105 minutes (input: 26.5 Ah). Discharge at 35 A for 36 minutes Output: 21.0 Ah).

Deep Cycling: Charge at 35 A for 1 hour, then cross over to a topping charge at 17 A for 2 hours (add distilled water if needed during the life of the cells). Discharge at 35 A to 1.0 v/cell.

# CAPACITY (Ah)

852	732	640	517	402	221	112	Cycle No.
		40.3(1) shorted on cycle 672	38.7(1)	40.2(1)	43.3 2 cells shorted on cycle 328 1 cell on cycle 344	42.8	Cellophane (4 cells)
		39.2(1) shorted on cycle 682	1) 35.8 1 cell shorted on cycle 414 another on 423 1) 40.2(2) 1 cell shorted on cycle 576 1) 39.2(1) shorted on cycle 687		44.5 ted 1 1 e 344	48.6	E-2291 (40/20) (no additive) (4 cells)
		43.7(1) shorted on cycle 730	39.9(1)	40.7(1)	40.2 2 cells shorted on cycle 328, 1 cell on cycle 352	48.0	E-2291 (40/20 (with additive) (4 cells)
44.8	39.3	44.4	41.5	42.4	47.8	48.2	K-306 (4 cells)
42.7	42.5	42.5	40.4	34.9	44.4	46.6	Celgard 3400 (4 cells)
45.1	42.4	41.5	42.5	43.0	47.6	47.5	1 Celgard 3400 + 1 Cellophane (4cells)
	41.7 all 3 cells shorted on cycle 797	41.3	42.0	42.5	44.5	46.0	1 E-6001 + 1 Cellophane (3 cells)
	0				1.0		

Table 4 - Life Cycling Data of the 3-4 Cell 35 Ah BB-600 Units (Cont)

3124	2931	2702	2512	2302	2143	1300	1735	1602	1502	1402	1302	1217	1123	1012	942	Cycle No.
																Cellophane (4 cells)
																E-2291 (40/20) (no additive) (4 cells)
																E-2291 (40/20) (with additive) (4 cells)
						The 3 K-3 damaged o cycler. separater	38.1	38.4	34.0	36.4(3)	38.8(3)	41.3(3)	44.0 1 cell shorted on cycle 1152	45.0	40.1	K-306 (4 cells)
						K-306 & 4 celgard 3400 cells we ed on cycle 2085 due to failure r. (the 3 composite cells, on a ster cycler are OK on cycle 2085	39.0	39.5	36.8	37.5	38.1	38.0	43.2 ted 52	44.3	40.1	Celgard 3400 (4 cells)
39.7*	39.4	40.8	39.6	41.1	39.6	The 3 K-306 & 4 celgard 3400 cells were damaged on cycle 2085 due to failure of cycler. (the 3 composite cells, on a separater cycler are OK on cycle 2085)	42.9	41.7	40.4	40.1	42.5	46.0	42.0	41.8	41.1	1 Celgard 3400 + 1 Cellophane (4 cells)
																1 E-6001 + 1 Cellophane ( 3 cells)

\*EQUIPMENT FAILED, DESTROYED ALL CELLS

#### 5. Results and Discussion of the Phase II Tests

Eight BB-433 batteries, two each per separator variation, were constructed, tested and shipped to USAERADCOM during the course of the contract. The check out test results of the six batteries are shown in this section, the separator variations being; a) standard on layer of cellophane, b) one layer of Celgard 3400 and c) one layer of Permion P-2291 (40/20).

The 35 ampere-hour 24 volt BB-433 vented nickel-cadmium aircraft batteries tested in this program were built to comply with the weight, volume and interface specifications of BB-433/U battery. The outer dimensions of the battery are shown in figure 26. Special features of this battery are; a) 19 BB-600 unit cells in nylon cases where the nylon covers are welded to the cases, b) heavy duty nickel plated copper terminals to which the nickel tabs of the electrodes are bolted, c) leak-proof compression terminal-to-case seals, d) a headspace of 1½ inches, e) thin high rate plates and 40 Ah of useable capacity.

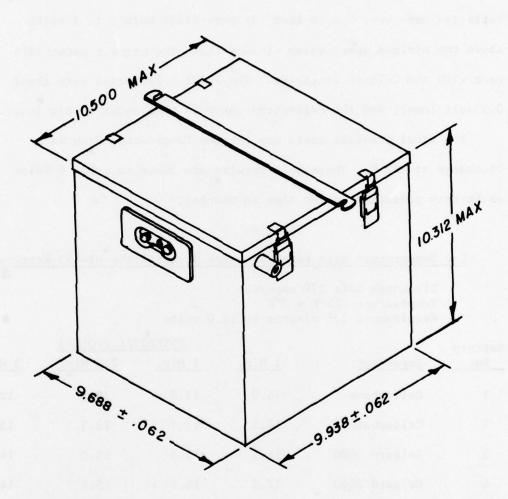
The capacity Discharge Test, for the three initial checkout cycles, are shown in table 5 below;

Table 5 - BB-433 BATTERY CAPACITY TESTS

Required Capacity in Ampere Hours to 20 V Cutoff - 35.0 Ah

Battery No.	Separator	Cycle 1	Cycle 2	Cycle 3
. 1	Cellophane	41.9	41.6	40.3
2	Cellophane	41.7	41.2	41.4
3	Celgard 3400	40.7	39.2	39.9
4	Celgard 3400	38.8	39.7	40.3
5	P-2291 (40/20)	37.9	39.9	39.7
6	P-2291 (40/20)	40.0	39.2	39.6

FIGURE 26
DIMENSIONS OF THE BB-433 BATTERY



After sucessfully meeting the initial capacity tests the batteries were checked out on the 20 second room temperature pulse test. The data are shown in figure 28, as battery potential versus time in seconds for the three 772 A, 20 second pulses. The IR drops of these batteries were very low in that the potentials were 3 to 5 volts above the minimum spec. value of 10 volts. The highest potentials were with the Celgard batteries. The Permion batteries were about 0.5 volt lower, and the cellophane controls were about 1 volt lower.

The final proveout tests was the Low Temperature High Rate Discharge at  $-22^{\circ}F$ . These test results are shown in table 6 below as battery potential versus time in minutes.

Table 6

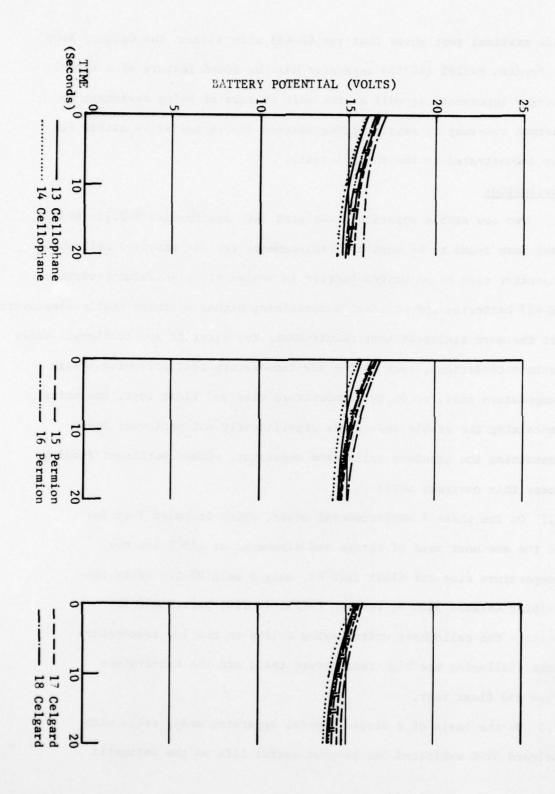
Low Temperature High Rate Discharge Tests of the BB-433 Battery

Discharge Rate 270 amperes Temperature  $-22^{\circ}F \pm 2^{\circ}F$  Requirement 2.5 minutes to 13.0 volts

Battery	POTENTIAL (VOLTS)							
No.	Separator	1 Min.	2 Min.	2.5 Min.	3 Min.			
1	Cellophane	14.0	13.8	13.0	12.0			
2	Cellophane	14.5	13.7	13.5	13.0			
3	Celgard 3400	16.5	15.5	15.0	14.0			
4	Celgard 3400	17.0	16.0	15.0	14.5			
5	P-2291 (40/20)	16.2	15.5	15.0	13.2			
6	P-2291 (40/20)	16.3	15.8	14.8	13.5			

The above tests show that the standard cellophane battery did barely meet the 13 volt spec on 2.5 minutes, whereas the Celgard and Permion batteries exhibited significantly high potentials at 3 minutes.

ROOM TEMPERATURE HIGH RATE PULSING TESTS OF THE EP BB-433 BATTERIES REGIME: 722 A for 20 Secs (rt) - 2 Min o.c. between pulses FIGURE 27



this critical test shows that the BB-433 with either the Celgard 3400 or Permion P-2291 (40/20) separator has the added feature of a lower battery impedance, as well as the main feature of being resistant to thermal run-away by separator degradation due to oxidative attack (as was demonstrated in the phase I test).

#### 6. Conclusions

Two new stable separators, Celgard 3400 and Permion P-2291 (40/20), have been found to be superior replacements for the standard cellophane separator used as an oxygen barrier in vented nickel-cadmium batteries.

BB-433 batteries and unit cells containing either of these stable separators met the most stringent test requirements for aircraft applications. Under certain conditions, such as the low temperature test following a high temperature test, or on the temperature rise and float test, the units containing the stable separators significantly out performed those containing the standard cellophane separator. Other pertinent findings under this contract were:

- 6.1 On the phase I environmental tests, which included 3 cycles at the one hour rate of charge and discharge at 125°F and the temperature rise anf float (120°F), only 5 cell BB-600 units containing Celgard 3400 or Permion P-2291 (40/20) passed all the tests the cellophane units having failed on the low temperature test (following the high temperature test) and the temperature rise and float test.
- 6.2 On the basis of a single layered separator wrap, cells with Celgard 3400 exhibited the longest useful life on the automatic

life cycling test, i.e., no shorts were encountered in the 4 cell Celgard 3400 group up to the 2085 cycles tested. By contrast, the 4 cell cellophane groups shorted out between cycles 328 and 672; that of Permion P-2291 (40/20) with no additives shorted out between cycles 414 and 682; and that of Permion with the stabilizing additives shorted out between cycles 328 and 730.

- 6.3 BB-600 groups with composite separator wraps (1 layer of Celgard 3400 plus 1 layer of cellophane and K-306, which is a Celgard substrate with a 0.1 mil coating of cellulose acetate) exhibited poor performance on the low temperature tests, but were outstanding on the life cycling tests; ie.e., none of the Celgard/cellophane cells failed up to the 3500 cycles tested and only one K-306 cell shorted (on cycle 1152) up to the 2085 cycles tested.
- 6.4 The phase II battery tests on BB-433 batteries containing (two each per variation) Celgard 3400 or Permion 2291 (40/20) were successful in terms of meeting the high rate environmental requirements.
- 6.5 Preliminary tests on the fadeout regime with 10 cell VNC 5.5 Ah cells indicate, that about 1% indium introduced by chemical impregnation into the sintered type cadmium anodes will significantly improve the low temperature performance of nickel-cadmium cells that had earlier been subjected to a prolonged high temperature overcharge regime.

The above conclusions indicate that, overall, Celgard 3400 is the best abailable, best-state-of-the-art single layered separator for the BB-433 aircraft battery, or other high rate vented

nickel-cadmium batteries. For applications requiring moderate rates of charge and discharge, such as for communications and electronics electronics equipment, the best separator wrap would be a combination of 1 layer of Celgard 3400 and 1 layer of cellophane (cellophane facing the anodes), with K-306 as a runner-up.

#### 7. REFERENCES

- O. Wagner, "Investigation of New Cell Components for Vented Nickel-Cadmium Batteries," Research and Development Technical Report ECOM-4364, Sep 1976.
- O. Wagner and D. Williams, "Investigation of Charging Methods for Nickel-Cadmium Batteries," Proc. of 26th Power Sources Symposium, May 1974.
- A. W. Goodman and L. L. Senderak, "MIL-B Environmental Testing of Twelve Nickel-Cadmium Aircraft Batteries," Report Brief, QEEL/C 74-73, Naval Ammunition Depot, Crane, Indian, April 1974.
- J. J. Lander, "Cold Temperature Testing of MIL-STD Nickel Cadmium Batteries with P-229l Separator Material," Interim Report, AFAPL/POE-74-7 (Air Force), April 1974.
- J.J. Lander, "Initial Performance Test on A7-D Nickel-Cadmium Aircraft Batteries for Inservice Life and Performance Test at Davis Montham AB", Test Report AFAPL-POE-75-I (Air Force) November 1974
- J.J. Lander and P.W. Schlfesser, "Thermal Runaway Test on Ni-Cd Aircraft Batteries Having Cellophane or P-229 Separators," Interim Report, AFAPL-POE-75-14 (Air Force Sep 1975.
- R. Hayaski, K. Feldman, J.L. Lockner, and T.E. King; "Experiments with Polypropylene Separators," Abstract No. 137, Extended Abstract of the Electrochemical Society Meeting, Toronto, Canada, May 1975.
- F.G. Will and H.J. Hess, "Cadmium Electrode Mechanism, Electrode Morpliology and Capacity" Final Report, Contract NAS 3-12967 (NASA) General Electric Corp. Research and Development; 15 March 1971.
- Y. Okinka, "Charge acceptance of Cadmium Hydroxide Electrodes at Low Temperatures", J. Electrochemical Soc. II7, 583 (1970).
- O. Wagner, "Secondary Cadmium Air Cells", J. Electrochemical Soc. II6, 693 (1969).
- II. A. Fleischer, U.S. Patent #2,771,499 (1956)

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